A Versatile Injector for the Gas Chromatograph

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A sample injector for a gas chromatograph has been designed which permits the injection of both liquid and solid samples and requires little if any modification of the injection port. In addition, the injector provides a closed system in which reactions can be carried out on a micro-scale before the reaction products are flushed onto the chromatograph.

The solid samplers which are presently available to the chromatographer can be grouped according to mode of operation. Generally solid samplers are modifications of injection syringes (1-6) or metal gauzes which are dropped or moved by a magnet (7-12) into the injection area. Others have used glass inserts (13,14), glass capillaries which are crushed (15) and systems which were designed for the specific instrument (16). Commerically available solid samplers have features which limit their use. Those which inject through the existing chromatographic septum are usually limited as to size of sample. Injection systems which include a pyrolysis oven are expensive, bulky and may require either extensive modification of the chromatograph or the purchase of accessory equipment. Those which drop samples into the injector area either in the form of a wire gauze or Teflon capsule must be dismantled occasionally to remove the used samplers. In addition, they are not suitable for gas chromatographs with horizontal injection.

The injector which is shown in Figure 1a can be easily fabricated from parts which are normally found in the laboratory. The injector acts as a device either for placing and removing solid samples in the carrier gas stream or through which liquid samples may be injected. It will operate repetitively, i.e., it does not require shut down between samples. It does not interrupt the gas flow; consequently, there is no disturbance in the baseline. The injector is adaptable to solid samples; both solids in solution, e.g., benzoic acid, and solid substrates, e.g., cheese, pepper and coffee. Although the injector was designed for on column injection, it will fit any chromatograph which has an injection port at least 3/32 in. in diameter. The injector will work satisfactorily either vertically or horizontally as long as the injection septum is thick enough to support the weight of the injector.

The injector consists of a 4 in. piece of 14 gauge (.083 in, o.d.) stainless steel hypodermic syringe tubing soldered to a stainless steel 1/8 in. to 1/16 in. Swagelok reducing union. The small end of the union must be drilled so the tubing will fit into the union. The 1/8 in. end of the union accommodates a glass injection port (Barber Colman part #A4574).* The tubing end of the injector is silver soldered to seal the end, using solder which will withstand the temperature of the flash heater. A window is cut into the side of

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**Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.*

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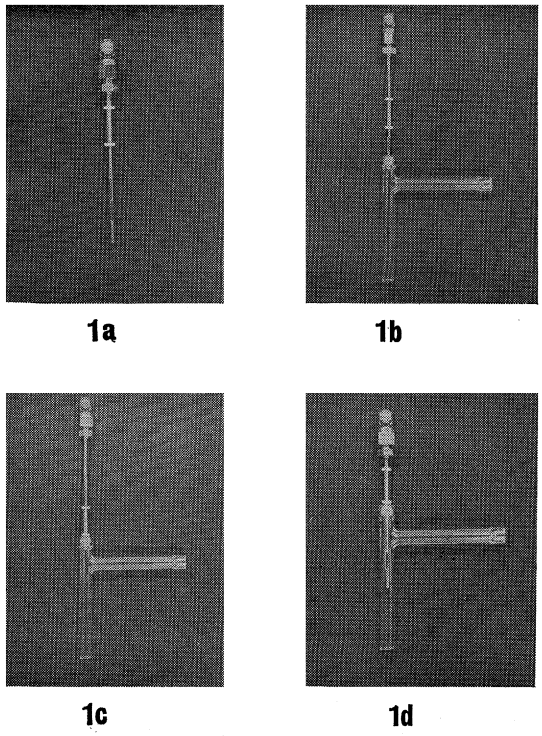

Figure 1a. The injector

1b. The injector in position. The tip of the injector is inserted into the septum.

1c. The injector in position. The Teflon sleeve is in place acting as a closure for the window.

1d. The injector in the injected position. In this position the flash heater will vaporize the sample and the carrier gas will sweep the sample from the injector.

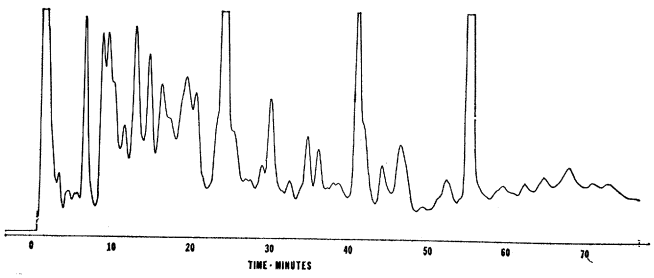

Figure 2. Gas chromatogram of the volatiles from 2 mg of used cigarette filter. Temperature programmed from 75° to 185° C at 2°/min.

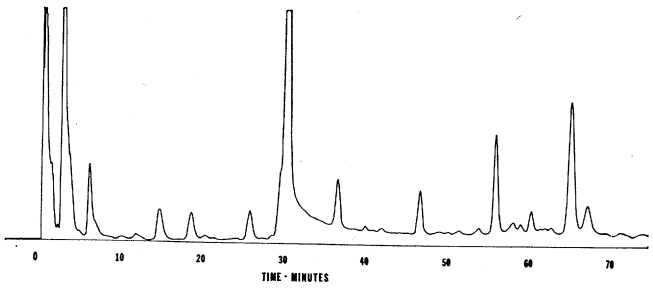

Figure 3. Gas chromatogram of the volatiles from 8 mg of Cheddar cheese. Temperature programmed from 90° to 185° C at 2°/min.

the injector by grinding on a 1/2 in. grinding wheel one-half way through the tubing. Four 1/32 in. holes are drilled into the back of the window to allow better exchange of gas. A sleeve made from a 1 in. length of 13 gauge standard wall Teflon tubing is slipped over the stainless steel tubing to act as a closure for the window. (The leakage around the Teflon sleeve is less than one ml per hr at 20 psi). Teflon washers, cut from a 1/4 in. rod or 1/16 in. sheet and drilled with a 3/32 in. hole are placed on both ends of the sleeve so that the sleeve can be more easily slid into place.

The injector is placed in the chromatograph by inserting approximately 1/2 in. into the injection septum (Figure 1b). This will require either replacing the injection septum with one which has a through hole or cutting a small hole to allow passage of the injector. The injector should fit snugly but slide without requiring excessive force. The injector will then accommodate any solid sample which will fit into the window of the injector. More conveniently, solid samples are packed into a 1/2 in. length of 1/16 in. glass capillary, lightly plugged with glass wool and placed in the window. This allows easy insertion and removal of the sample and prevents contamination of the injector. After the sample is inserted, the system is closed by sliding the Teflon sleeve over the window (Figure 1c). Injection of the sample is accomplished by pushing the injector into the injection port (Figure 1d). As the injector is pushed in, it slides through the Teflon sleeve. The pressure of the sleeve against the injection septum provides a tight seal against gas leakage. The sample when in place will be vaporized by the heat of the flash heater and swept onto the column by the carrier gas flowing over the injector. When withdrawing the injector, tweezers must be used to hold the Teflon sleeve tight against the septum while sliding the injector through it. This is best accomplished by applying adequate pressure to the top Teflon washer while holding the stainless steel tubing with the tweezers. The injector must be withdrawn quickly but carefully so that it is not pulled completely from the chromatograph. The sleeve can then be lifted and the spent sample removed.

Figures 2 and 3 are chromatograms of 2 samples which were injected in this manner. The chromatograph was a Barber Colman Model 5000 with on column injection. The column was U-shaped, 6 ft x 1/4 in., 7.5% ethylene glycol adipate + 2% H_3PO_4 on Anakrom ABS, and temperature programmed as indicated. The injection port temperature was 220°C.

Liquid samples or samples in solution can be injected with equal facility two different ways. A piece of glass capillary filled with glass wool can be placed in the window, the sample adsorbed onto the glass wool and then injected into the carrier gas stream. The liquid sample may also be injected by pushing the empty injector into the injected position and injecting through the upper septum using a syringe with a 4 in. needle. Figure 4 shows chromatograms comparing an injection in the normal manner and an injection through the injector using a 4 in. needle.

Two examples of the reactions that have been carried out in this laboratory using the injector are

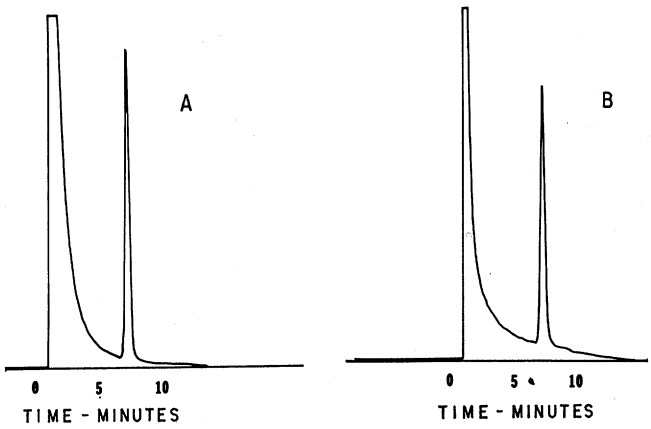

Figure 4. Gas chromatogram of benzoic acid injected in the normal manner (A) and injected through the injector using a syringe with a 4 in. needle (B).

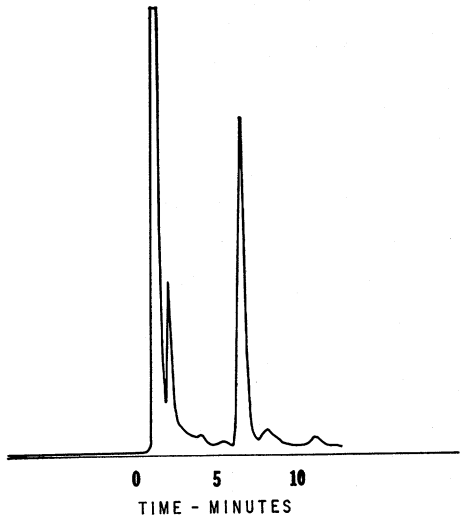

Figure 5. Gas chromatogram of nonanal obtained by the regeneration of nonanal 2,4-dinitrophenylhydrazone by the addition of 50% CH_3SO_3H.

regeneration of 2,4-dinitrophenylhydrazones and liberation of acids from their salts. Many 2,4-dinitrophenylhydrazones are easily regenerated by reaction with acid and heat (17,18). The derivatives in solution can be absorbed on a small plug of glass wool or on a small column of Celite and Seasorb 43, the solvent removed and the derivative acidified and injected. Methane sulfonic acid is preferred to other acids for carrying out reactions in the injection port. Inorganic acids (sulfuric, hydrochloric and phosphoric acid) are too caustic and dilutions of them make poor solvents for organic materials. Regeneration of 2,4-dinitrophenylhydrazones was often incomplete using these acids, and the chromatographic peaks showed shoulders. Methane sulfonic acid regenerates the compounds completely and gives single symmetrical peaks for all compounds investigated (Figure 5).

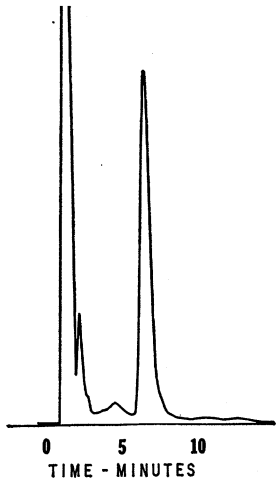

Figure 6. Gas chromatogram of propionic acid obtained after acidification of acid salt with 50% CH_3SO_3H.

Acid salts can be acidified in the injector and peaks obtained for the volatile fatty acids. The fatty acids can be trapped as salts on a short column of Celite impregnated with potassium bicarbonate (19) or a salt solution can be absorbed onto glass wool, acidified and injected. To prevent the loss of sample in liberating volatile fatty acids, the acid salt should be acidified after the sample is placed in the window and the Teflon sleeve slid into place. In this case the acid must be added through the top of the injector using a syringe with a 4 in. needle. Since the Teflon sleeve is transparent, the tip of the syringe needle can be observed in applying the acid to the top of the capillary. Figure 6 is a chromatogram of propionic acid obtained after the acidification of the acid salt on Celite impregnated with $KHCO_3$.

The capability to place some of the reactants in the injector, closing the injector, and adding other reactants before flushing the reaction products onto the gas chromatograph enables the gas chromatography of volatile compounds which would normally be lost during the reaction or subsequent manipulation. The method of carrying out reactions either in the injection port or just prior to injection may open up a new area for gas chromatographic analysis. ■